MILLIMETER-MILLIMETER-WAVE DOUBLE-MODULATION DOUBLE-RESONANCE SPECTROSCOPY

OLIVER ZINGSHEIM, LUIS BONAH, HOLGER S. P. MÜLLER, FRANK LEWEN, SVEN THORWIRTH, STEPHAN SCHLEMMER, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*.

Complex organic molecules (COMs) show regularly very rich spectra, sometimes at a line density close to the confusion limit. The plethora of lines often originates from the presence of different conformers and/or low-lying vibrational states. The analysis of spectra may considerably be further complicated by vibration-rotation or other interactions. However, accurate spectroscopic predictions in the millimeter-wave (MMW) region are essential for identifying molecules in space. Double-resonance techniques can help to solve these challenges.

We present first MMW−MMW double-resonance (DR) spectra to unambiguously assign weak and perturbed rotational lines of propanal (C_2H_5CHO). As already shown in chirped pulse Fourier transform microwave (CP-FTMW)[a] and in MW−MMW DR experiments,[b] the Autler-Townes splitting[c] allows for distinguishing between regressive or progressive energy level schemes. The Autler-Townes splitting is clearly visible in our 2D spectra. Furthermore, implementation of a double-modulation double-resonance (DM-DR) technique, pulse modulation of the pump and frequency modulation of the probe source, allows for confusion- and baseline-free spectra containing only the line(s) of interest. We discuss details of the observed Autler-Townes splitting, benefits of simplified spectra, and possible future applications, such as automatization.

[a] D. Schmitz et al., *J. Phys. Chem. Lett.* **6** (2015) 1493

[b] K. M. Roenitz et al., *J. Phys. Chem. A.* **122** (2018) 6321

[c] S. H. Autler and C. H. Townes, *Phys. Rev.* **100** (1955) 703